NAVAL AIR WARFARE CENTER AIRCRAFT DIVISION
PATUXENT RIVER, MARYLAND

TECHNICAL REPORT

REPORT NO: NAWCADPAX/TR-2000/16

DEGREE OF CURE, HEAT OF REACTION, AND VISCOSITY OF 8552 AND 977-3 HM EPOXY RESIN

by

S. J. Ng
R. Boswell
S. J. Claus
F. Arnold

10 March 2000

Aerospace Materials Division
Air Vehicle Department
Naval Air Warfare Center Aircraft Division
Patuxent River, Maryland

and

A. Vizzini
Aerospace Engineering Department
University of Maryland
College Park, Maryland

DEPARTMENT OF THE NAVY
NAVAL AIR WARFARE CENTER AIRCRAFT DIVISION
PATUXENT RIVER, MARYLAND

NAWCADPAX/TR-2000/16
10 March 2000

RELEASED BY:

17 Feb 2000
ROLAND COCHRAN / DATE
Head, Polymer Composites and Materials Branch

3/10/00
DALE MOORE / DATE
Director, Materials Competency
Naval Air Warfare Center Aircraft Division

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
10 March 2000	Technical Report	

4. TITLE AND SUBTITLE

Degree of Cure, Heat of Reaction, and Viscosity of 8552 and 977-3 HM Epoxy Resin

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

S. J. Ng
R. Boswell
S. J. Claus
F. Arnold

A. Vizzini
Aerospace Engineering Department
University of Maryland

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Air Warfare Center Aircraft Division
22347 Cedar Point Road, Unit #6
Patuxent River, Maryland 20670-1161

8. PERFORMING ORGANIZATION REPORT NUMBER

NAWCADPAX/TR-2000/16

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Naval Air Systems Command
47123 Buse Road Unit IPT
Patuxent River, Maryland 20670-1547

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The heat of reaction, degree of cure, and viscosity of Hexcel 8552 and Cytec Fiberite 977-3 HM neat resins were measured using a modulated differential scanning calorimeter and a rheometric digital analyzer. Expressions were developed using isothermal tests for correlating the rate of degree of cure and the viscosity with the degree of cure using a Lee, Loos, and Springer approach. The models were exercised to predict the kinetic behavior of the resins using respective manufacturer cure cycles. Data were collected and good correlation was found with the model. In addition, kinetic behaviors of these systems were compared to Hercules 3501-6 data. A second study was also performed to investigate cure models developed based on neat and prepreg forms of the resin. Vastly different viscosity behaviors were found indicating further physical insights are necessary to account for fiber/resin content and material properties difference.

15. SUBJECT TERMS

Degree of Cure
Viscosity
Heat of Reaction
Epoxy Resins

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Stanley Ng
Unclassified	Unclassified	Unclassified	UL	22	19b. TELEPHONE NUMBER (include area code) 301-757-2338

ABSTRACT

The heat of reaction, degree of cure, and viscosity of Hexcel 8552 and Cytec Fiberite 977-3 HM neat resins were measured using a modulated differential scanning calorimeter and a rheometric digital analyzer. Expressions were developed using isothermal tests for correlating the rate of degree of cure and the viscosity with the degree of cure using a Lee, Loos, and Springer approach. The models were exercised to predict the kinetic behavior of the resins using respective manufacturer cure cycles. Data were collected and good correlation was found with the model. In addition, kinetic behaviors of these systems were compared to Hercules 3501-6 data. A second study was also performed to investigate cure models developed based on neat and prepreg forms of the resin. Vastly different viscosity behaviors were found indicating further physical insights are necessary to account for fiber/resin content and material properties difference.

CONTENTS

ACKNOWLEDGMENT

This work was supported by NAVAIRSYSCOM, NAVSTO Office, Patuxent River, Maryland, with Mr. Mo Devillier. The author would also like to thank Mr. Grant Cooper at BHTI for providing the viscosity data on the five-ply 8552 laminate.

INTRODUCTION

Analytical models describing cure kinetics of thermosetting resins have been developed in recent years (references 1 and 2) and accurately predict processing behavior of fiber-reinforced organic matrix structures. More advanced thermosetting resins for prepreg applications have been developed in recent years. These new materials offer higher strength, stiffness, and damage tolerance for structural applications. Two newer epoxy resins are studied in this report: Hexcel 8552 and Cytec Fiberite 977-3 HM. To describe these resins analytically, their kinetics behaviors are studied in this report and compared to Hercules 3501-6.

EXPERIMENTAL PROCEDURE

The heat of reaction and the degree of cure were measured using a modulated differential scanning calorimeter (MDSC). A neat resin sample ranging from 8 to 12 mg was encapsulated in a standard aluminum sample pan. The encapsulated sample was placed on an MDSC sample platform under isothermal temperature conditions in a nitrogen environment of 50 ml/min flow rate and applying a modulated temperature of ±1.5°C cycle every 60 sec from the sample was measured as a function of time. For 8552 resin, isothermal tests were performed at 140°C, 150°C, 160°C, and 170°C, while dynamic test was performed from 100°C to 280°C at the rate of 3°C/min. For 977-3 HM resin, isothermal tests were performed at 160°C, 170°C, 180°C, and 200°C, while dynamic test was performed from 100°C to 280°C at the rate of 3°C/min. The following expressions from the Lee, Loos, and Springer approach were used (reference 1).

The total heat of reaction, H_R, was calculated by the expression:

$$H_R = \int_0^{tf} \left(\frac{dQ}{dt}\right) dt \tag{1}$$

where t_f is the time required to complete the reaction during dynamic heating.

The amount of heat, H, released up to time t was determined using the rate of heat generation measured during the isothermal scanning experiments. The rate of heat generation was plotted versus time and the area under the curve provided the amount of heat released:

$$H = \int_0^{t} \left(\frac{dQ}{dt}\right) dt \tag{2}$$

The degree of cure, α, is defined as:

$$\alpha = \frac{H}{H_R} \tag{3}$$

The rate of degree of cure, $d\alpha/dt$, is calculated by the expression:

$$\frac{d\alpha}{dt} = (\frac{dQ}{dt}) / H_R \qquad (4)$$

where the rate of heat generation dQ/dt is provided by the measurements.

The viscosity measurements for 8552 and 977-3 resin were made using a Rheometric Dynamic Analyzer II (RDA II) using aluminum parallel plates. The radius of the plates was 25.0 mm and the gap between the plates was 0.8 mm. The disc oscillated at 1.0 Hz while 5% strain was applied. The viscosity was measured at 140°C, 150°C, 160°C, and 170°C for Hexcel 8552 resin, and 150°C, 160°C, 170°C, 180°C, and 200°C for Cytec Fiberite 977-3 resin. Viscosity measurements for 8552 and 977-3 HM were also made based on optimal cure schedule provided by the manufacturers.

RESULTS AND DISCUSSION

GENERAL

Data measuring the rate of heat generation, dQ/dt, were generated in dynamic scanning experiments. The total heat of reaction of the resin was determined using Equation 1 and gave the following values:

H_R=497 J/g (Hexcel 8552) (5)
H_R=362 J/g (Cytec Fiberite 977-3 HM)
H_R=473.6 J/g (Hercules 3501-6 HM) (reference 1)

DEGREE OF CURE

The degree of cure and the rate of degree of cure were determined from the results of the isothermal scanning experiments. From the measured values of dQ/dt, the heat released H up to time t, the degree of cure at time t, and the rate of degree of cure $d\alpha/dt$ at time t were calculated using equations (1) through (4). Measured results are shown as data points in figure 1.

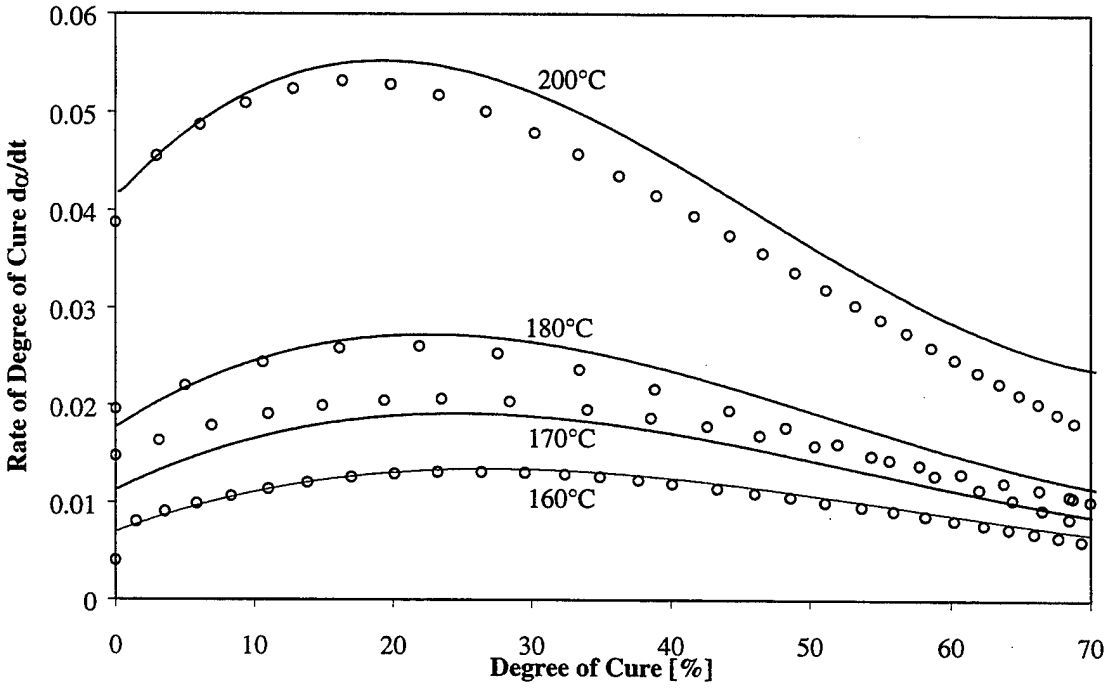

Figure 1: Rate of Degree of Cure Versus Degree of Cure for 977-3 Resin at Various Isothermal Conditions

In this investigation, the following cubic expression was found to describe the data well:

$$\frac{d\alpha}{dt} = K_1\alpha^3 - K_2\alpha^2 + K_3\alpha + K_4\alpha \tag{6}$$

where

$$K_i = A_i exp(-\Delta E_i/RT), \quad i=1,2,3,4 \tag{7}$$

In equations (6) and (7), A_i are preexponential factors, ΔE_i are the activation energies, R is the universal gas constant, and T is the absolute temperature. The constants K_i were obtained by fitting a cubic least squares curve to the $d\alpha/dt$ versus α data. The values of A_i and ΔE_i were found by fitting straight lines to the natural logarithmic values of K_i versus $1/T$ using equation (8). The values of these constants are listed in table 1. The model is exercised, and the calculated values are compared with the measured data, as illustrated in figure 1. It is interesting to note that the model does not fit perfectly for isothermal conditions, despite the model was obtained from the data measured at the exact same temperatures. This is due to the mathematical

curve fit determination of the activation energy constants, and the preexponential constants are based on four sets of temperature data. This average effect will give a close approximation to some of the measured data, but not for the entire set of data obtained originally.

$$\ln(K_i) = \ln(A_i) + (\frac{-\Delta E_i}{R})\frac{1}{T}, \qquad i=1,2,3,4 \tag{8}$$

Table 1: The Values of the Constants in Equation (6) for 8552 and 977-3 Resin

	3501-6 (reference 1)	**8552**	**977-3 HM**
A_1 [sec^{-1}]	3.50×10^{7}	1.67×10^{3}	1.64×10^{5}
A_2 [sec^{-1}]	3.36×10^{7}	-5.15×10^{3}	-2.19×10^{4}
A_3[sec^{-1}]	3.27×10^{3}	1.04×10^{7}	1.90×10^{2}
A_4[sec^{-1}]	0	0	1.02×10^{5}
ΔE_1 [J/mol]	8.07×10^{4}	5.09×10^{4}	6.92×10^{4}
ΔE_2 [J/mol]	7.78×10^{4}	5.70×10^{4}	6.00×10^{4}
ΔE_3 [J/mol]	5.66×10^{4}	9.07×10^{4}	4.61×10^{4}
ΔE_4 [J/mol]	0	0	7.60×10^{4}

VISCOSITY

Sampled measured values of viscosity μ as functions of time of 977-3 HM resins are shown in figure 2. Because the degree of cure α is also a function of time, the viscosity can also be expressed in terms of α.

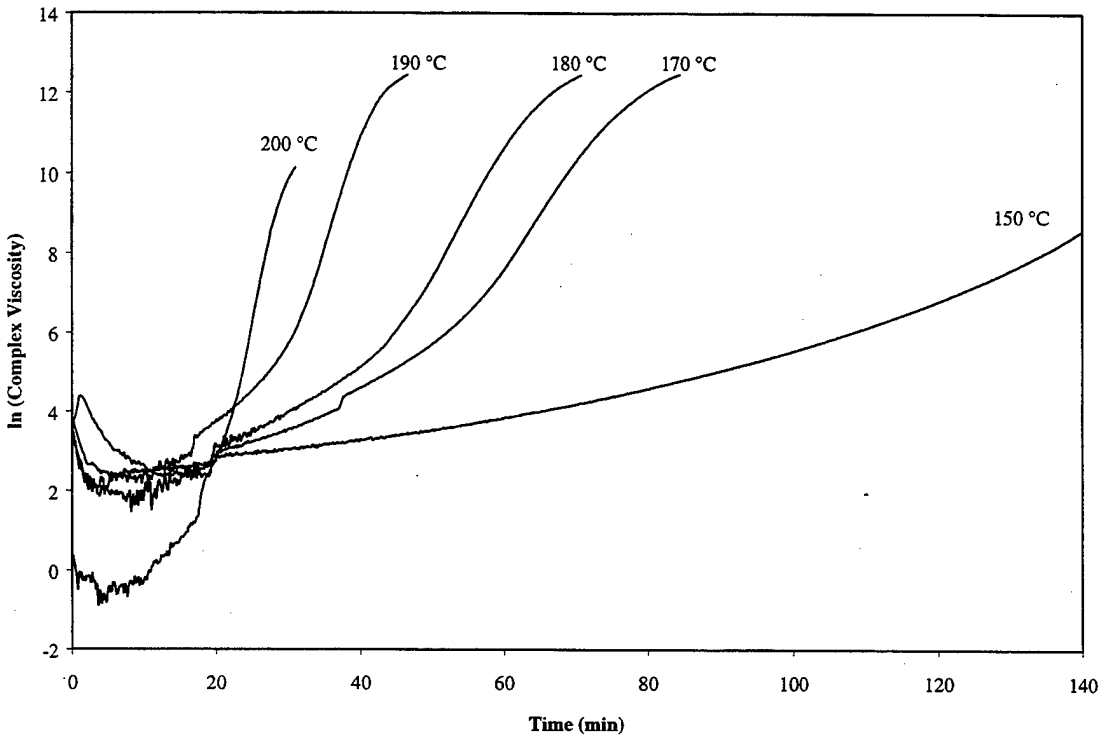

Figure 2: Measured Isothermal Viscosity as a Function of Time for 977-3 HM

An expression was sought to correlate the data given in figure 2. The following equation was found to represent the data:

$$\mu = \mu_\infty \exp(U / RT + K_1\alpha^2 + K_2\alpha) \qquad (9)$$

where μ_∞ is a constant, U is the activation energy for viscosity, K_1 and K_2 are constants independent of temperature. To determine the constants, equation (9) was written in the form:

$$\ln \mu = \ln \mu_\infty + U / RT + K_1\alpha^2 + K_2\alpha \qquad (10)$$

where

$$A = \ln \mu_\infty + U / RT$$

The constants K_1, K_2, and A parameters were found by fitting a quadratic least square curve to the μ versus α data generated at a constant temperature. Values K_1 and K_2 are listed in table 2. The values of A are plotted as a function of the inverse of the absolute temperature. A linear least square fit to A values versus 1/T data provided the values of μ_∞ and U listed in table 2.

Table 2: The Values of the Constants in Equation (8) for 8552 and 977-3 Resin

	3501-6 [1]	8552	977-3 HM
K_1	14.1	25.49	11.10
K_2	0	-1.32	0.81
μ_∞ [Pa-s]	7.93×10^{-14}	8.83×10^{-5}	3.46×10^{-5}
U [J/mol]	9.08×10^{4}	4.91×10^{4}	4.62×10^{4}

CURE CYCLE SIMULATION

Kinetics prediction models of 8552 and 977-3 HM have been developed in the previous sections based on isothermal tests and measurements. Applicability of these isothermal models to nonisothermal heating conditions, i.e., manufacturer cure cycle, are important in terms of manufacturing/processing perspective. Standard manufacturer's cycles for both 8552 and 977-3 were used to test the accuracy of isothermal-based models. The degree of cure and viscosity results for 8552 resin results are presented in figures 3 and 4, respectively. As shown in figure 3, the degree of cure model was used to simulate the two-step manufacturer cure cycle up to the second dwell period at 178°C. Measured data are represented by dots, and the model prediction by a straight line. The degree of cure model calculation was performed based on measured time and temperature at every 6 sec. At each temperature, $d\alpha/dt$ was calculated using equation (4) by numerical integration. Good correlation was found between the model and the measured data. The model slightly underestimates the measured data between $0.05 > \alpha > 0.18$, and overestimates the measured data between $0.75 > \alpha > 0.82$. The slight variation could be due to the change in temperature setting at the end of the first step (90 min), of the cure cycle, and the beginning of the second step (130 min).

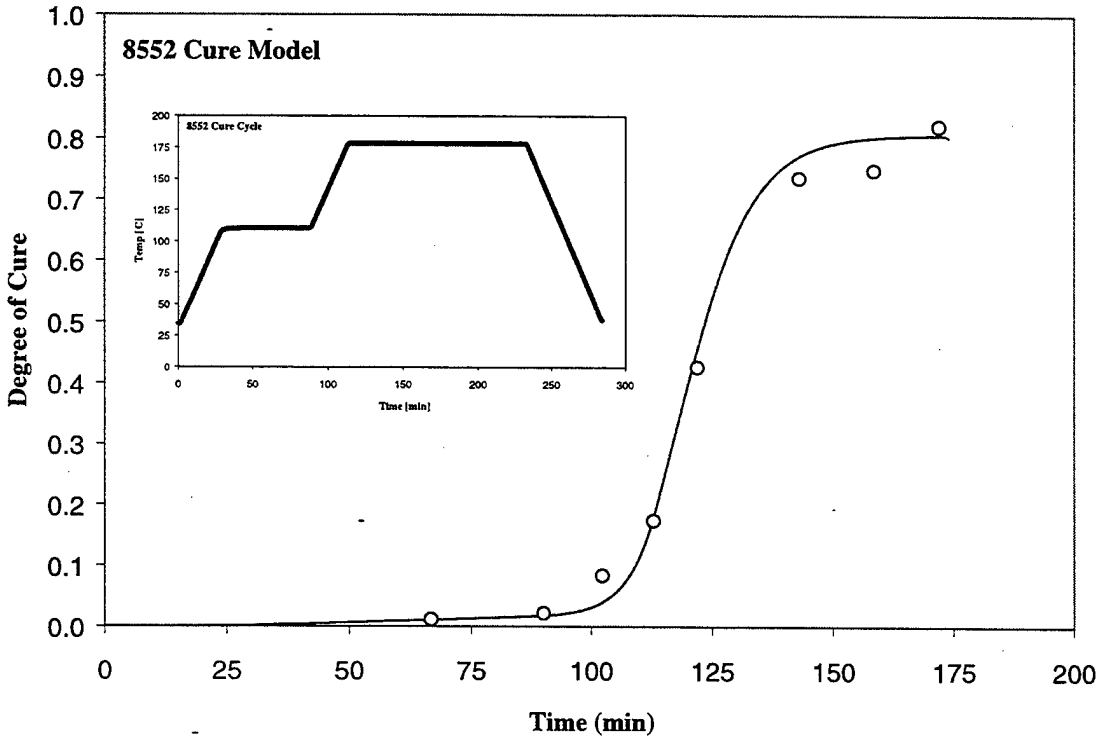

Figure 3: Degree of Cure Modeling of 8552 Resin Based on Manufacturer Cure Cycle

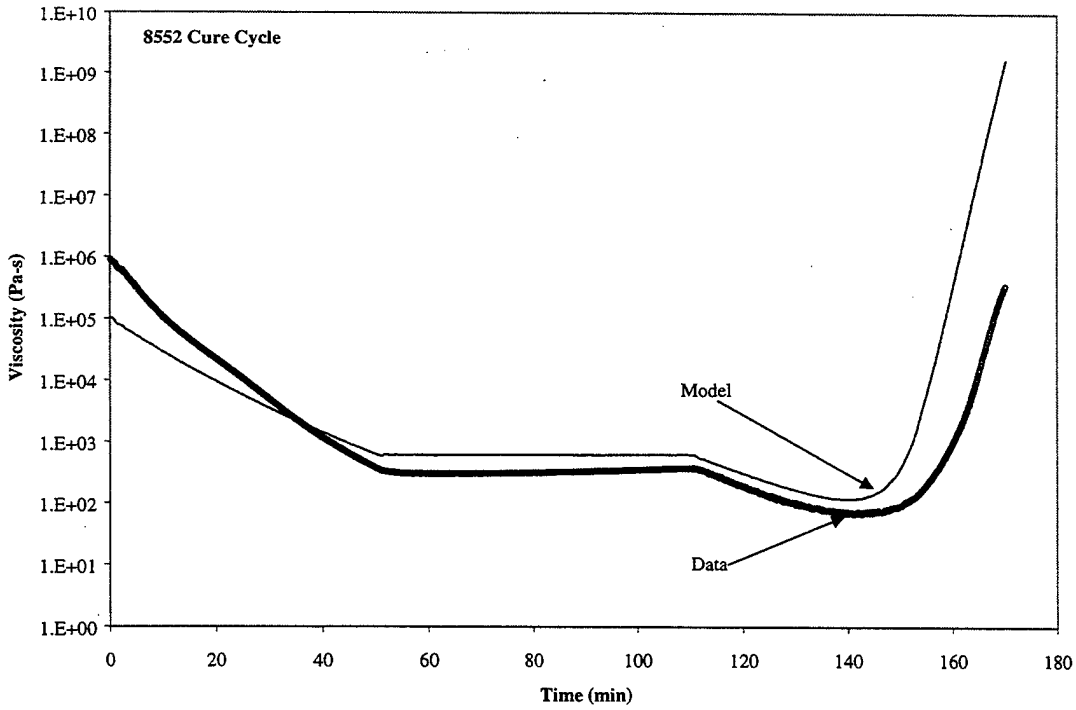

Figure 4: Viscosity Modeling for Hexcel 8552 Based on Two-Step Manufacturer Cure Cycle

From the known values of temperature (T) and the degree of cure (α), viscosities (μ) based on the model developed were calculated using equation (7), and compared to rheological measurements. The results are presented in figure 4. As shown in figure 4, the viscosity of the resin decreases during the initial ramp, then hold constant during the first dwell period at a lower temperature. After undergoing the second ramp and during the second dwell period, the resin reaches a minimum point of viscosity suitable for compaction and crosslinking to take place. Further addition of heat increases the degree of cure and viscosity dramatically. The rheological data measured agreed well with model prediction to the minimum point of viscosity of the resin. However, the model overestimates the measured data after $\alpha > 0.5$ (140 min), at which point the viscosity rises as the mobility of the resin is increasingly restricted by intermolecular crosslinking. This difference could be due to accumulated error in the finite difference mathematical approach used in isothermal models to predict nonisothermal behavior of 8552. It is notable that most isothermal models reviewed (references 1 and 2) do not predict the rheological behavior during initial heating and after resin gelation very well, which generally occurs when the thermoset matrix is 40-60% crosslinked. Similar procedures were performed for 977-3 HM, and the results obtained are shown in figure 5. The 9773-HM viscosity profile is based on a one-step cure cycle. Good agreement was also found between the data and the model developed. Slight differences due to similar reasoning were also observed during the initial heat up (0-20 min) and after the resin reaches gelation (after 85 min).

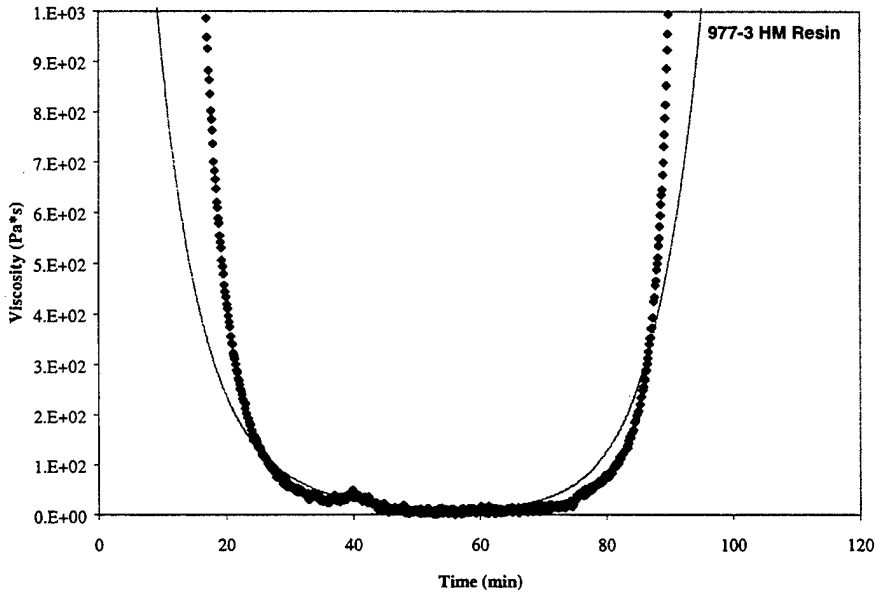

Figure 5: Viscosity Modeling of 977-3 HM Based on One-Step Manufacturer Cure Cycle

PREPREG AND NEAT RESIN MEASUREMENTS

A second study was conducted to investigate the effect of using prepreg and neat resin for investigation of viscosity behavior of resin. 8552 neat resin model was used to compare data to a five-ply laminate S2/8552 system. The results are shown in figure 6. As illustrated in figure 6, the viscosity profile of the laminate and the neat resin reveals similar rheological behavior during the cure cycle. However, the isothermal model based on neat resin underestimated the viscosity magnitude for about 10^2 pa-s before gelation. The results indicate the fiber volume has a significant effect in the measurement of the resin flow properties. In a standard rheometer with parallel plates, resin viscosity measurements are made based on the strain developed when a torsional load is applied. When a laminate is used for this type of measurement, the fiber will rotate along with the resin during the cure. As the viscosity of the resin begins to decrease, the fiber becomes relatively stiff compared to the resin, and acts as a dry friction source when the parallel plates rotate. Therefore, it is reasonable that a laminate will always give a higher measured viscosity than a neat resin sample. Consideration should be given to which viscosity measurement is more suitable for modeling a specific type of composite processing problems.

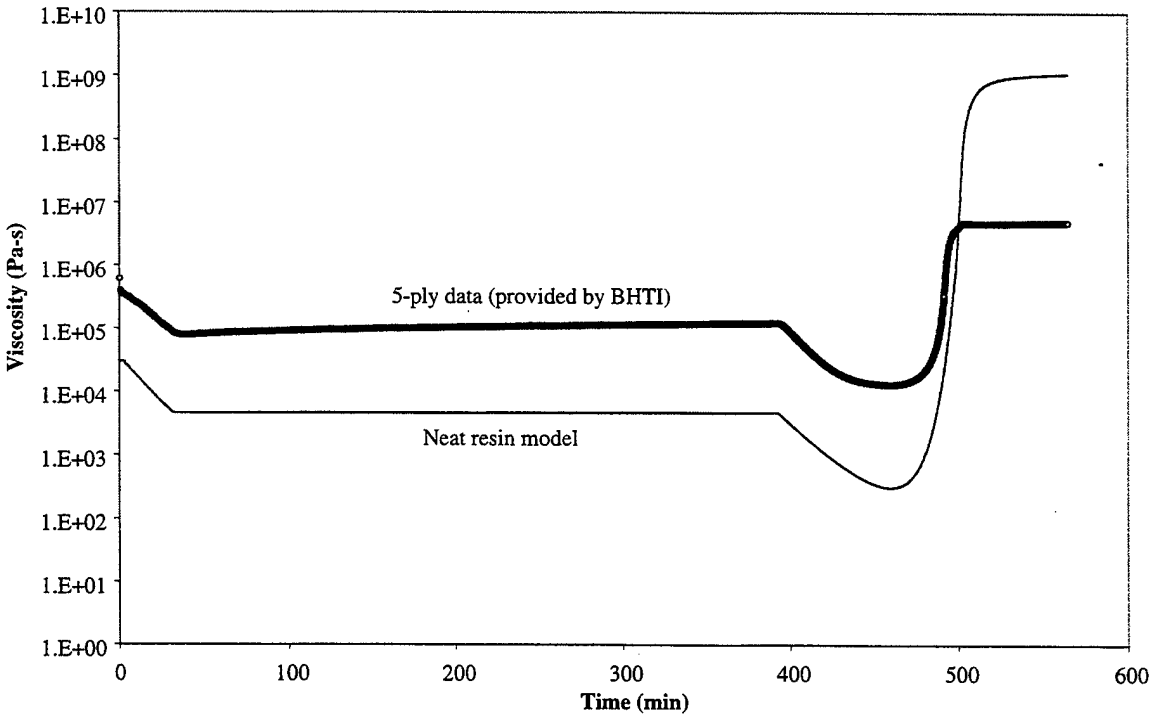

Figure 6: Viscosities Measurements of 8552 Resin in Neat and Prepreg Form

THIS PAGE INTENTIONALLY LEFT BLANK

CONCLUSIONS

Analytical models for predicting degree of cure and viscosity of 977-3 HM and 8552 resins have been developed based on isothermal thermal analysis techniques. The resin models can be used to model the cure process of fiber reinforced composites employing 977-3HM and 8552 resins using constants determined from this study and as listed in tables 1 and 2, respectively. These models were validated using standard manufacturer recommended cure cycles. Results indicate good correlation to experimental measurements. A second study was also performed to investigate cure models developed based on neat and prepreg forms of the resin. The viscosity measurements based on prepreg forms were significantly higher, up to 10^2 times, compared to the neat resin prediction. The results indicate that the presence of fiber as a reinforced composites constituent plays an important role acting as a source of dry friction during the rheological measurement. Special consideration should be taken when choosing the type of measurement to be used in modeling viscosity of a resin-based material.

THIS PAGE INTENTIONALLY LEFT BLANK

REFERENCES

1. Lee, W. I., Loos, A. C., and Springer, G.S., "Heat of Reaction, Degree of Cure and Viscosity of Hercules 3501-6 Resin", J. Composite Materials, Vol. 16, 1982, pp. 510-520.

2. Ciriscioli, P. R. and Springer, P., Smart Autoclave Cure of Composites, Technomic Publishing Company, Lancaster, Pennsylvania, 1990.

THIS PAGE INTENTIONALLY LEFT BLANK

DISTRIBUTION:

NAVAIRWARCENACDIV Patuxent River, MD (4.3.4.3)	(16)
NAVAIRWARCENACDIV Patuxent River, MD (Technical Publishing Team)	(1)
University of Maryland Aerospace Engineering Department College Park, MD	(1)
DTIC	(1)